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13. ABSTRACT *(Maximum 200 words)*

Composite materials for application on Naval aircraft must possess certain unique characteristics including toughness, resistance to temperature and moisture, and high specific strength. Two resin systems being investigated for potential airframe applications include Phthalonitrile and PETI-5. Both are addition systems with high temperature applications. Thermogravimetric analysis (TG) and modulated differential scanning calorimetry (MDSC) were used to determine the glass transition temperatures (Tg) before and after thermal heat treatment as well as to determine thermal decomposition kinetics. Both resin systems were autoclaved cured but it was found that the Phthalonitrile resin needed an additional post cure at 375°C for 8 hours in order to maximize mechanical properties. Decomposition kinetics were utilized to investigate the effect of post cure Phthalonitrile compared to the standard autoclave cure.

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THERMAL CHARACTERIZATION OF TWO EPOXY SYSTEMS

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INTRODUCTION

Composite materials for application on Naval aircraft must possess certain unique characteristics including toughness, resistance to temperature and moisture, and high specific strength. Two resin systems being investigated for potential airframe applications include Phthalonitrile and PETI-5. Both are addition systems with high temperature applications. Thermogravimetric analysis (TG) and modulated differential scanning calorimetry (MDSC) were used to determine the glass transition temperatures (T_g) before and after thermal heat treatment as well as to determine thermal decomposition kinetics. Both resin systems were autoclaved cured but it was found that the Phthalonitrile resin needed an additional post cure at 375°C for 8 hours in order to maximize mechanical properties. Decomposition kinetics were utilized to investigate the effect of post cured Phthalonitrile compared to the standard autoclave cure.

KINETIC METHODS OF ANALYSIS

Dynamic and isothermal methods (*1*) were employed to obtain kinetic data by TG. The heating rates were 0.2, 0.5, 1.0, 2.0, 5.0, 10.0 °C/min. Dynamic thermal decomposition kinetics were determined according to equation 1;

$$\frac{d\log\beta}{d(1/K)} = 0.457E/R \qquad (1)$$

where β is the heating rate, E is the activation energy, R is the gas constant (8.314 J/mol/K), T is the absolute temperature and 0.457 is a constant (first approximation). A plot of the log heating rate verses the reciprocal of the absolute temperature at a constant conversion will have a slope of 0.457 E/R. The Arrhenius frequency factor is then calculated from equation 2.

$$A = \frac{\beta E}{RT^2}\frac{E}{RT} \qquad (2)$$

A relationship between activation energy and estimated useful lifetime of a material at a given percent conversion and temperature was developed by Toop (*2*). His equation (3) is;

$$t_f = \frac{E}{RT_f} + \ln[\frac{E}{\beta R} P \frac{E}{RT_c}] \quad (3)$$

where t_f = estimated time to failure, T_f = failure temperature (K),

$$P(\frac{E}{RT}) =$$

value from a numerical integration table, T_c = temperature from an operator selected weight loss such as 5-20% at a selected heating rate.

For isothermal kinetics five temperatures were chosen in order to obtain the Arrhenius plot. A plot of the Δ % weight change versus the reciprocal of the absolute temperature will have the slope E/R. The rate equation is used to analyzed the data,

$$\ln k = \ln A - \frac{E}{RT} \quad (4)$$

where k is the rate constant and A is the Arrhenius frequency factor. Once E and A are known and assuming a first order equation, k may be calculated. The activation energies and rate constants are used to compare post cured and non-post cured Phthalonitrile resin. If the analysis shows an increase in the activation energy and a decrease in the rate constant this would represent an increase in thermal stability due to the post cure.

THERMOGRAVIMETRY

TG curves analyzed under a nitrogen atmosphere for the post cured Phthalonitrile are shown in Figure 1. The curves are displaced to the right indicating higher temperature as the heating rate increases from 0.2 to 10°C/min. Constant percent conversions from 5 to 20% are also displayed in Figure 1. Figure 2 shows the Arrhenius plot for the various conversions; the slopes are parallel which indicates that the decomposition mechanisms are similar. The kinetic values for the activation energy and frequency factor support this; thermal stability data is listed in Table 1. From Table 1 the post cured Phthalonitrile shows an average activation energy at the 5 and 10% conversion of 209 kJ/mol. The non post cured shows an average activation energy of 125 kJ/mol for the same conversions. The post cured Phthalonitrile has a higher activation energy and a lower rate constant which indicates a significant improvement in its thermal stability. Isothermal TG kinetics were used to confirm the variable heating rate method for the post cured Phthalonitrile. The isothermal temperatures investigated were 430, 450, 500, 520 and 530 °C. Figure 3 shows a typical thermograph at 530 °C after 150 minutes; the Phthalonitrile only lost approximately 6.5% of its original weight. Figure 4 is an Arrhenius plot for the isothermal runs. This shows excellent agreement with the variable heating rate kinetics; the activation energy was found to be 205 kJ/mol. Figure 5 is a overlay of both the standard autoclave and post cured Phthalonitrile;

thermal stability is evident for the post cured sample which does not show a weight loss until approximately 400 °C. Both samples were heated to 900 °C, but the autoclaved cured has a much higher percent weight loss: greater than 50% compared to the post cured at less than 40% . This is attributed to an increase in thermal stability associated with the triazine structure.

Variable heating rate kinetics were also employed for PETI-5. Figure 6 is a typical thermograph at a heating rate of 0.2 °C/min under a nitrogen atmosphere. PETI-5 exhibits similar thermal properties as Phthalonitrile; both resins exhibit high thermal stability where degradation does not occur until after 400 °C. For PETI-5, the activation energy ranges from 200 to 248 kJ/mol at 5 to 25% conversion, thermal stability data is listed in Table 2. Figure 7 is the lifetime plot for PETI-5. As with the Phthalonitrile, PETI-5 has excellent high temperature thermal properties at 300 °C.

MODULATED DIFFERENTIAL SCANNING CALORMETRY

To measure the glass transition temperature (T_g), MDSC was employed using a TA Instruments 2920 DSC. The modulated parameters were 3.0 °C /min heating rate with 1.5 °C modulation at 80 sec. The autoclaved cured Phthalonitrile T_g was approximately 160 °C . Once this material was conditioned by post curing the T_g increased to the resin's decomposition temperature. Figure 8 is an overlay of both the Phthalonitrile samples; the autoclaved cured sample displays a distinctive step at160 °C in the reversing heat flow. This T_g step is not evident with the post cured sample.

PETI-5 resin has its T_g at 165 °C under the same condition, but due to the limitations of this paper the thermograph is not displayed. After post-cure, the T_g of PETI-5 increased to approximately 250°C.

CONCLUSION

The thermal data reveals that the two resin systems are excellent for high temperature applications. The kinetic results show the activation energies and frequency factors for thermal decomposition are similar. For the Phthalonitrile sample, post curing at 375 °C for 8 hours increases the thermal stability and brings its T_g up to the decomposition region. With post curing, Phthalonitrile activation energy increased from 110 to 125 kJ/mol. PETI-5 resin decomposition kinetics are similar to the Phthalonitrile; its activation energies were 200 to 217 kJ/mol for the 5 and 10% conversion respectively. For aircraft applications, the requirement for T_g is that it must be 50 °F above the operational temperature; these resins could fulfill the high temperature requirements in many locations on the aircraft.

REFERENCE

1. ASN/ASTM E-698-79
2. D.J. Troop, IEEE Trans. Elec. Ins E-1-6,2 (1971)

TABLE 1.

THERMAL STABILITY OF PHTHALONITRILE
AUTOCLAVE AND POST CURED

	% CONVERSION	ACTIVATION ENERGY (kJ/mol)	log FREQUENCY FACTOR (min^{-1})	RATE CONSTANT (at 300°C) (min^{-1})
AUTOCLAVE	5	125.3	7.606	$1.51X10^{-4}$
	10	125.1	7.522	$1.26X10^{-4}$
	20	129.2	7.704	$8.20X10^{-5}$
AVERAGE		126.5		
POST CURE				
	5	209.7	12.29	$1.5X10^{-7}$
	10	208.4	11.94	$8.3X10^{-8}$
	20	234.6	13.43	$1.0X10^{-9}$
AVERAGE		217.6		
ISOTHERMAL		204.5	12.0	$2.12X10^{-7}$

TABLE 2.
THERMAL STABILITY OF PETI-5

% CONVERSION	ACTIVATION ENERGY (kJ/mol)	log FREQUENCY FACTOR (min^{-1})	RATE CONSTANT 300°C (min^{-1})
5	200.5	10.97	$4.7X10^{-1}$
10	217.2	11.95	$1.3X10^{-8}$
15	233.4	12.91	$4.0X10^{-9}$
20	248.2	13.78	1.4410^{-9}

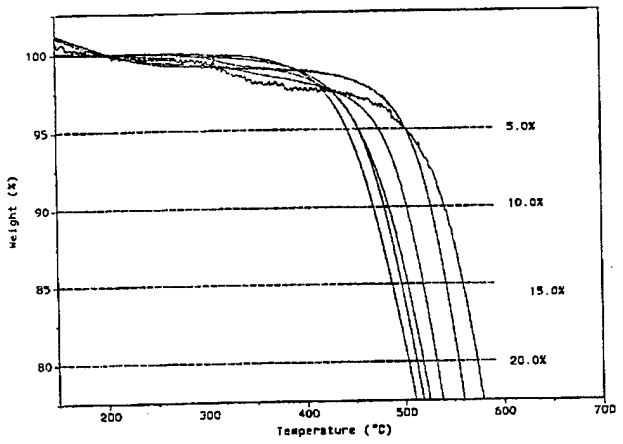

Figure 1 – TG curve of Phthalonitrile, Post-Cure at various heating rates and conversions

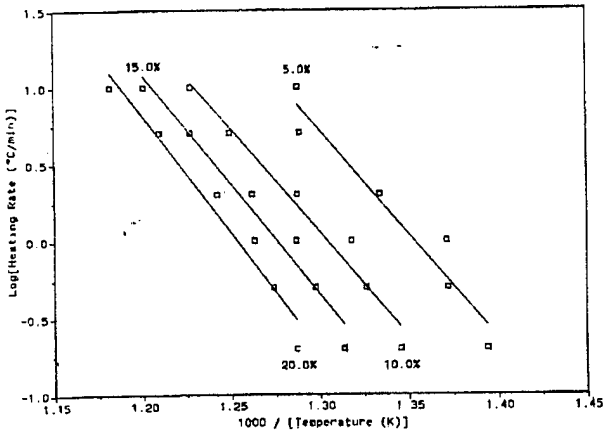

Figure 2 – Arrhenius Plot of Phthalonitrile, Post-Cure at various conversions

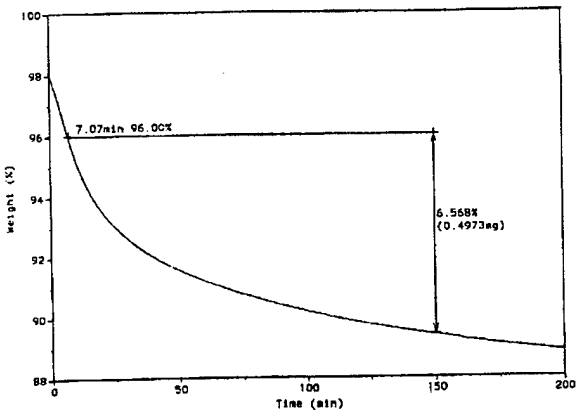

Figure 3 – Isothermal TG of Phthalonitrile, Post-Cure at 530 °C

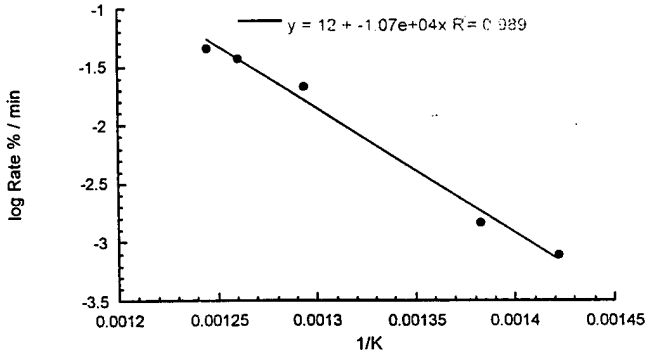

Figure 4 – Arrhenius Plot of Isothermal TG
data for Phthalonitrile Post-Cure; E_A= 204.6 kJ/mol

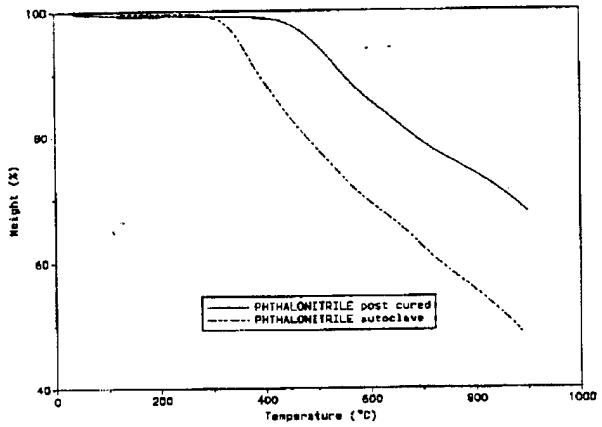

Figure 5 – Phthalonitrile Autoclaved & Post-Cured TG Curve at 0.2 °C/min

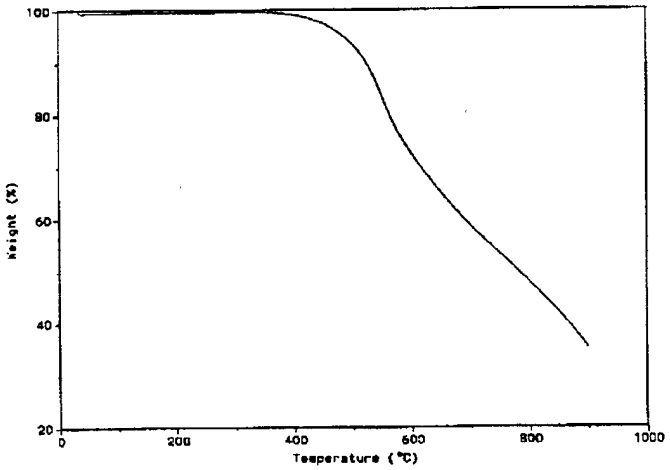

Figure 6 – PETI-5 TG curve at 0.2 °C/min

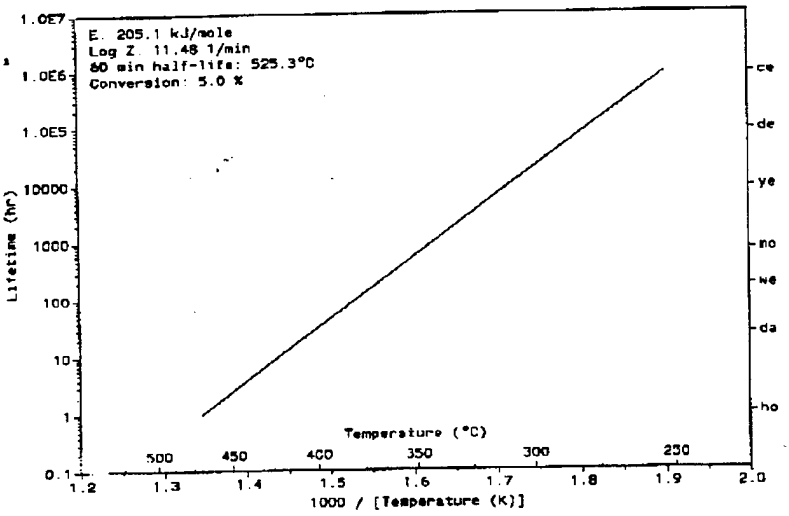

Figure 7 – Lifetime Plot of PETI-5

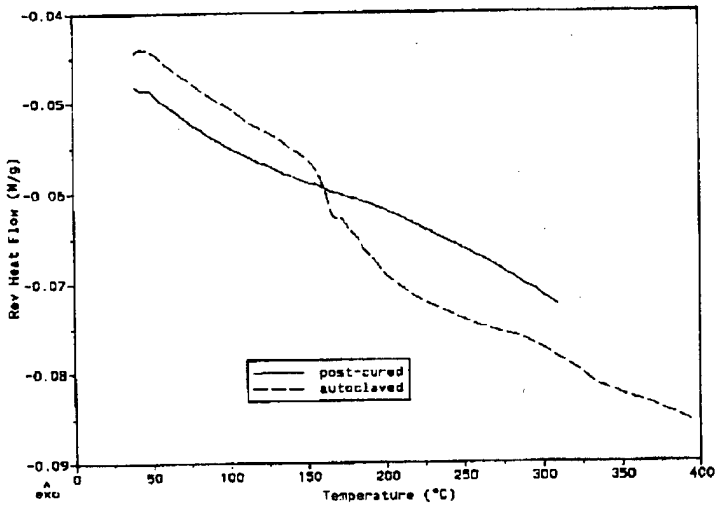

Figure 8 – MDSC of Phthalonitrile Autoclaved and Post-Cured